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Copper Keplerates: High-Symmetry Magnetic Molecules

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Keplerates are molecules that contain metal polyhedra that describe both Platonic and Archimedean solids; new copper keplerates are reported, with physical studies indicating that even where very high molecular symmetry is found, the low-temperature physics does not necessarily reflect this symmetry.

Very high symmetry is both aesthetically appealing and a useful chemical trait to allow detailed physical studies. In the area of molecular magnetism this can be essential, for example to allow full treatment of magnetic behaviour, without making approximations required by the size of matrices,^[1] or over parameterisation of low-symmetry problems.^[2] One classic example is the study of the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ icosidodecahedron,^[3] where each edge of the massive paramagnetic cage is identical, allowing the observation of phenomena associated with frustration effects originating from the regular triangular arrange-

ment and the antiferromagnetic exchange interactions between adjacent Fe^{III} ions.^[3]

Keplerates are one class of high-symmetry molecules; the term refers to polymetallic compounds where some of the metals lie on the vertices of a Platonic solid (e.g. cube, octahedron, tetrahedron, icosahedron) and the others on the vertices of an Archimedean solid (e.g. a cuboctahedron). While keplerates have been recognised by Müller^[3] for polyoxometalates, they have not generally been recognised for 3d-metal cage complexes, although previous examples exist.^[4] Here we report a series of copper keplerates, and the physical studies thereof.

Two families of copper keplerates have been synthesised by mixing two different copper starting materials under diverse reaction conditions (see the Supporting Information, SI, for full experimental details). Comparison of all cages shows these to contain a $\{\text{Cu}_{12}\}$ cuboctahedron surrounded by platonic solids (Figure 1, SI). The first family involves a $\{\text{Cu}_{12}\}$ encapsulated in a cube of metals, and includes $[\text{Cu}_{12}\text{Mg}_8(\mu_3\text{-OH})_{24}(\text{OAc})_{12}(\text{H}_2\text{O})_{12}](\text{NO}_3)_4$ (**1**)^[5a] and $[\text{Cu}_{20}(\mu_3\text{-OH})_{24}(\text{OH})_4(\text{O}_2\text{CtBu})_8(\text{NH}_2\text{iPr})_8(\mu\text{-NH}_2\text{iPr})][\text{O}_2\text{CtBu}]_4 \cdot [\text{Cu}_{20}(\mu_3\text{-OH})_{24}(\text{O}_2\text{CtBu})_8(\text{NH}_2\text{iPr})_8(\mu\text{-NH}_2\text{iPr})][\text{O}_2\text{CtBu}]_8$ (**2**),^[5b] which crystal-

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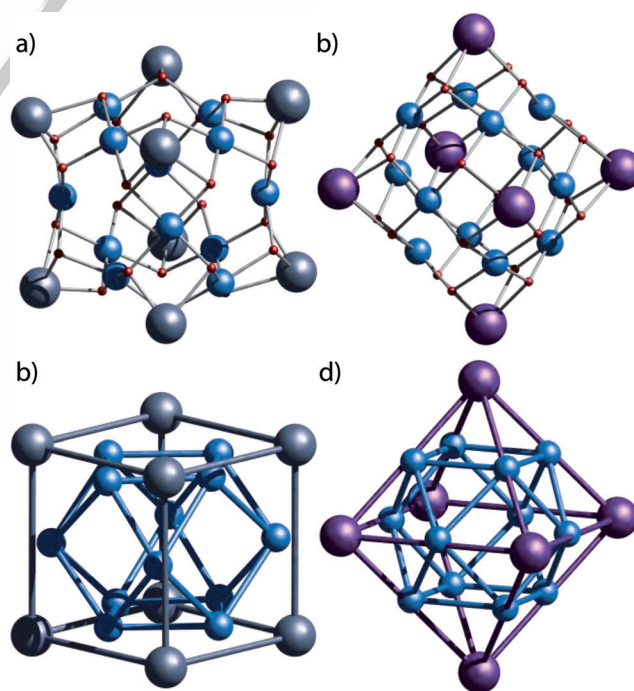


Figure 1. a, b) Metal core of $\{\text{Cu}_{12}\text{M}_8\}$ where $\text{M} = \text{Mg}^{\text{II}}$, **1** and Cu^{II} , **2** c, d) $\{\text{Cu}_{12}\text{Eu}_8\}$ **3**. Colour code: Cu, pale blue; Eu, purple; grey balls represent external $\{\text{M}_8\}$ formed by either Mg or Cu ions. ■ ■ OK? ■ ■ ■

lie in the $Pnnm$ and $\bar{P}1$ space groups, respectively. If considering the metal core alone, both compounds have O_h symmetry. The second family comprises a $\{\text{Cu}_{12}\}$ cuboctahedron encapsulated in an octahedron of europium, with molecular formula $[\text{Cu}_{12}\text{Eu}_6\text{Al}_6(\mu_3\text{-OH})_{18}(\text{OH})_{12}(\mu_4\text{-O})_6(\mu_3\text{-OH}_2)_6(\text{O}_2\text{CtBu})_{18}]$ (**3**),^[5c] these keplerates crystallise in the cubic space group, $Im\bar{3}d$.

The structures of these molecules are remarkably similar. In all cases the angles of the triangles within the cuboctahedron are in the range of $54.83(1)$ to $64.2(3)^\circ$ compared with the 60° required for a perfect cuboctahedron, whilst the angles between the copper squares range from $85.20(2)$ to $96.56(2)^\circ$. The $\text{Cu}\cdots\text{Cu}$ contacts between copper $\{\text{Cu}_3\}$ triangles and $\{\text{Cu}_4\}$ squares within the cuboctahedron are also largely invariant, ranging from $3.000(2)$ to $3.455(6)$ Å and $3.000(2)$ to $3.680(2)$ Å, respectively. The $\{\text{M}_3\}$ cubes which encapsulate the $\{\text{Cu}_{12}\}$ unit in **1** and **2** show little distortion from the ideal polyhedra; in **1** the $\text{Mg}\cdots\text{Mg}$ distances along the edges of the cube vary from $5.730(5)$ – $5.899(5)$ Å, with $\text{Mg}\cdots\text{Mg}\cdots\text{Mg}$ angles at the corners of the cube being in the range $89.85(7)$ – $90.15(7)^\circ$. In **2** $\text{Cu}\cdots\text{Cu}$ distances vary from $5.4350(8)$ – $5.9862(8)$ Å, with $\text{Cu}\cdots\text{Cu}\cdots\text{Cu}$ angles in the range $85.41(1)$ – $95.80(1)^\circ$. Similarly, the octahedron encapsulating the $\{\text{Cu}_{12}\}$ moiety in **3** displays a regular arrangement with $\text{Eu}\cdots\text{Eu}\cdots\text{Eu}$ angles of $59.36(1)$ to $60.32(1)^\circ$ and $\text{Eu}\cdots\text{Eu}$ distances $6.969(1)$ to $7.036(1)$ Å.

In **1** and **2** the $\{\text{Cu}_{12}\}$ cage is held together by twenty-four $\mu_3\text{-OH}^-$ ions, whilst in **3** eighteen $\mu_3\text{-OH}^-$ and six $\mu_4\text{-O}^{2-}$ ions complete the metal–oxygen core (Figure S1–6). Twelve disordered $\mu\text{-MeCO}_2^-$ groups (2.11 in Harris notation)^[6] and twelve terminal H_2O molecules complete the coordination spheres of the metal ions in **1**, whilst eight 2.11 tBuCO_2^- ligands and monodentate NH_2iPr and H_2O molecules are present in **2**. Both cages have disordered solvent/template molecules at their centres (see the SI for full details), H_2O in **1** and NH_2iPr in **2**. In compound **3** there are a total of eighteen pivalates displaying two distinct coordination modes, 3.21 and 1.11 (Figure S5), six Al^{III} ions with a disordered NH_2iPr in the central cavity of the cage. There are close contacts between cages in the extended structures of all three compounds (Figure S1–6). In **1** the cat-

ions pack in a brickwork-like fashion with the closest intermolecular interactions being between O-atoms ($\text{O}\cdots\text{O}$, ~ 3.4 Å) on neighbouring acetate/water molecules on the corners of the cubes. Compounds **2** and **3** pack in a similar fashion to **1** with the closest intercluster $\text{O}\cdots\text{O}$ interactions being ~ 5.4 Å and ~ 5.0 Å, respectively; the larger distances in the latter compounds being due to the presence of bulkier carboxylates.

Despite the large nuclearity of these cages, the presence of just $S=1/2$ spin centres permits calculation of their magnetic properties. The $4f^6 \text{Eu}^{\text{III}}$ ion is diamagnetic at low temperature, and its contribution can therefore be excluded under these conditions. We first discuss the magnetism theoretically predicted for a simple cuboctahedron of spins $S=1/2$ with one antiferromagnetic nearest-neighbour coupling.^[7] Such a system would be interpreted using the Heisenberg model, and as Figure 2 shows the zero- or low-field susceptibility rises as a function of temperature from zero to the paramagnetic limit. Since the theoretical ground state of the perfect cuboctahedron is a singlet, one observes steps in the zero- or low-temperature magnetization, which are caused by successive ground state level crossings. For frustrated Heisenberg systems the magnetization steps are often non-regular.^[7] The expected behaviour of $\{\text{Cu}_{20}\}$ (**2**) should be qualitatively similar, since it also features antiferromagnetic interactions in corner- and edge-sharing triangles.

Experimentally, this is not observed. In all three cases the $M(H)$ measurements are very similar; rather than the predicted step features a smooth, gradual increase in M with increasing field is seen, even at the lowest temperatures. This behaviour could not have been expected since—as the left-hand sides ■ ■ OK? ■ ■ of Figures 3 and Figure 4 show— $\chi_m T$ rises very slowly and therefore the exchange interactions are expected to be of the order of at least 50 K.

For such large antiferromagnetic exchange interactions the magnetization steps should be clearly observable. This is demonstrated in Figure 3, where the susceptibility data of **1** at higher temperatures can be reproduced by assuming a nearest neighbour exchange interaction of $J = -50$ K, but the magneti-

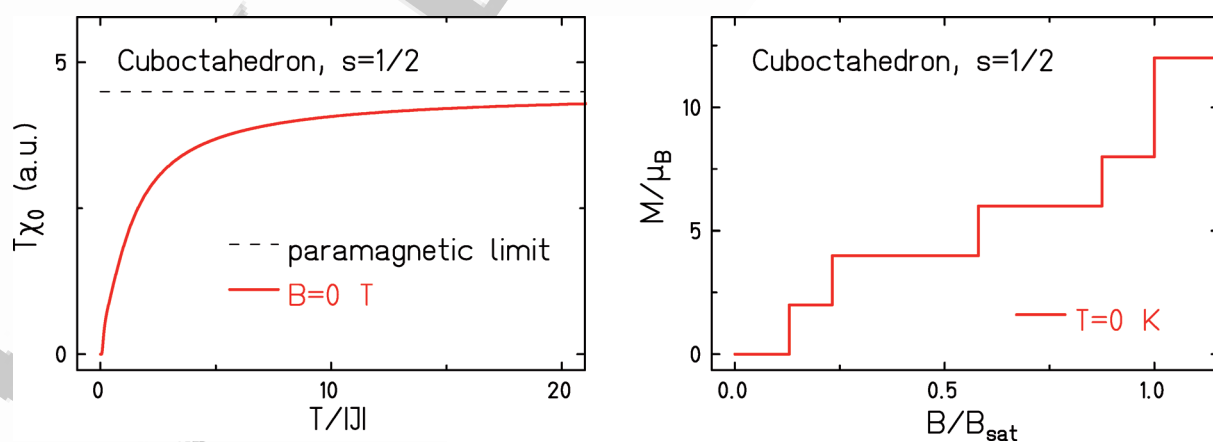


Figure 2. Theoretical zero-field magnetic susceptibility and zero-temperature magnetization of a regular cuboctahedron with antiferromagnetic coupling between nearest-neighbour spins.

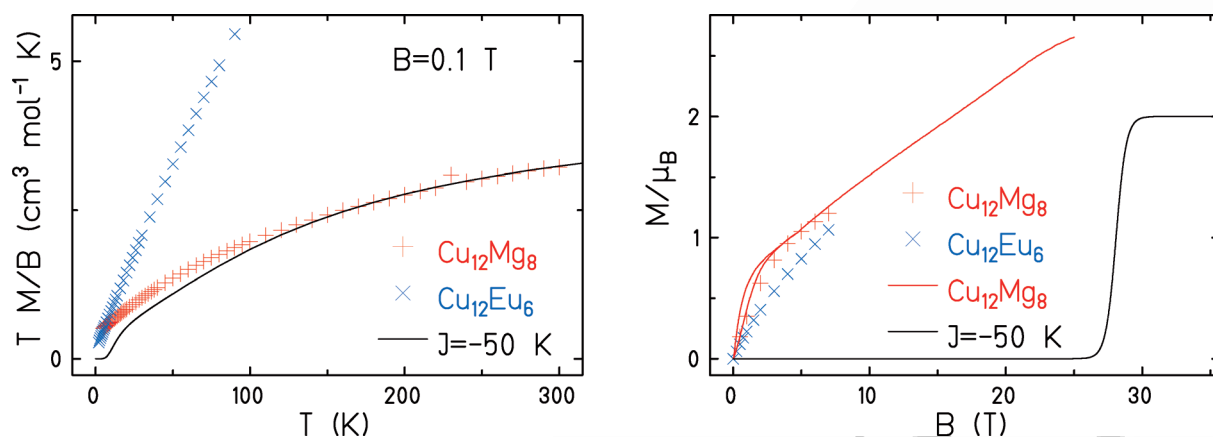


Figure 3. Left: experimental (symbols) and theoretical (curve) low-field magnetic susceptibility of **1** and **3**. Right: experimental low-temperature magnetization of **1** (+ symbols, $T = 2 \text{ K}$; red curve, $T = 0.5 \text{ K}$) and **3** (x symbols, $T = 1.8 \text{ K}$) as well as theoretical magnetization (black curve). ■■OK?■■

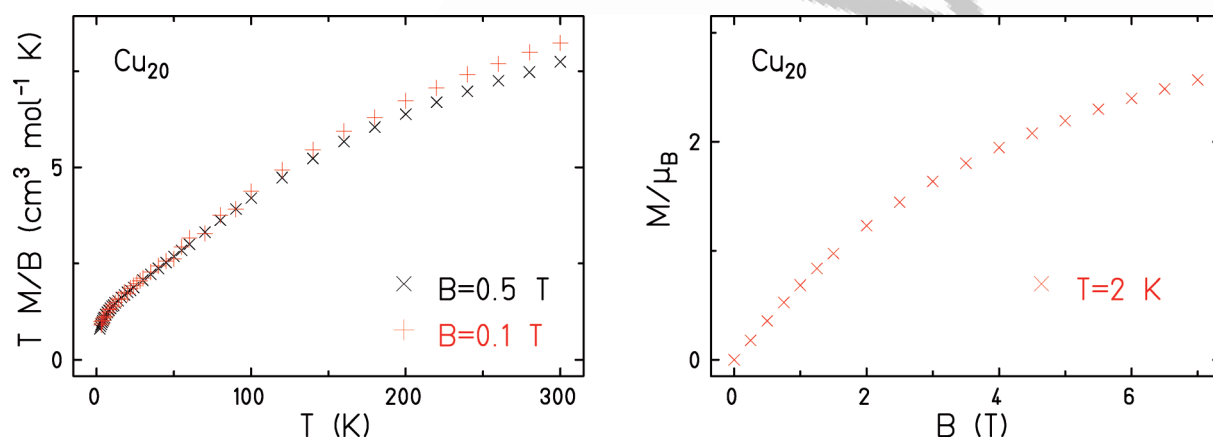


Figure 4. Experimental low-field magnetic susceptibility and low-temperature magnetization of $\{\text{Cu}_{20}\}$.

zation curve for such a big exchange would clearly feature a first magnetization step at a high field due to the large singlet-triplet gap. The slow rise of the magnetization is compatible with a large exchange constant, the loss of steps and the curvature at low fields are not. Possible contamination with isolated Cu^{II} ions cannot explain this behaviour, and it is not observed by EPR spectroscopy (Figure S7–S9). Our attempts to fit variable temperature $\chi_m T$ and magnetization data have been unsuccessful. We note that similar magnetic behaviour has been observed in another recently reported copper cluster.^[8]

The experimental magnetic properties are reminiscent of other keplerates, where the low-temperature magnetization together with other low-temperature observables cannot be described by a Hamiltonian that is of the assumed high symmetry of the cluster.^[9] Schröder et al. reported that the magnetism in some of those cases could be rather well fitted by employing a random distribution of exchange interactions. Herringer et al. show for a different compound that such randomness could be caused by orientational disorder of ligands.^[10] The same is true for disorder of counter ions or solvent molecules. In addition it is possible that highly symmetric structures rearrange at very low temperatures to lower symmetry, though

a variable temperature X-ray study of complex **1** revealed no structural changes to $T = 30 \text{ K}$. We would also like to remark that it is very well possible that the modifications are correlated in one molecule, that is, not random, but different from molecule to molecule. On the level of the discussed observables this could not be distinguished from true randomness.

Specific heat (C) data are shown in Figure 5. As the theoretical curve on the right-hand side ■■OK?■■ demonstrates, C should display a double-peak structure at $B = 0$. However, measurements show a broad, smeared out, magnetic specific-heat anomaly, at least for temperatures larger than the experimental base temperature (ca. 0.3 K). This behaviour implies that the magnetic specific heat should extend up to relatively high temperatures, thus superimposing with the nonmagnetic lattice specific heat. Nonetheless, the underlying intermolecular interactions are not relatively strong, as revealed by the field-dependent specific heat. The applied-field value of 1 T is already sufficient for narrowing and increasing the magnetic anomaly, while shifting it towards higher T , that is, for partially decoupling such interactions. Note that relatively broad contributions to the specific heat could be explained as due to a distribution of the exchange values or to the presence of short-

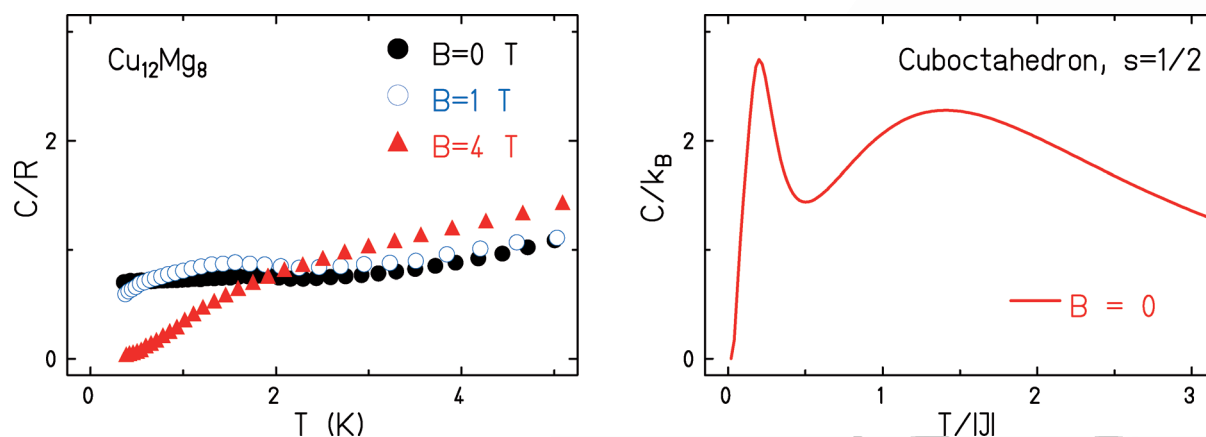


Figure 5. Experimental (the data for 1 is shown on the left) and theoretical specific heat (right) of $\{Cu_{12}\}$.

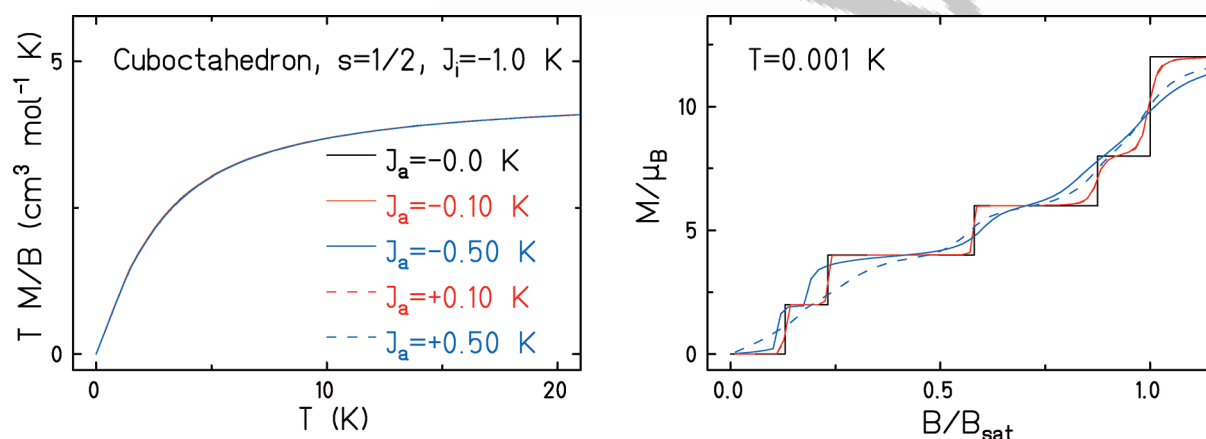


Figure 6. Theoretical low-field ($B = 0.1$ T) magnetic susceptibility and low-temperature ($T = 0.001$ K) magnetization of a regular cuboctahedron with anisotropic symmetric exchange between nearest-neighbour spins.

range intermolecular magnetic correlations, though no clear three-dimensional ordering is observed here.

With the experimental data in mind, we have investigated the following scenarios: anisotropic symmetric exchange, anti-symmetric, that is, Dzyaloshinskii–Moriya (DM) exchange, random exchange as well as intermolecular interactions as possible sources of the observed deviation from an ideal cuboctahedron. Figure 6 shows the powder-averaged calculations for a setting where in addition to an isotropic Heisenberg exchange J_i , an anisotropic but symmetric exchange J_a is added. For simplicity the anisotropic component is chosen along the direction of the bond connecting two interacting spins in the cuboctahedron. Such interactions are active in the heavier 4d and 5d elements, such as ruthenium or osmium.^[11] As one can see the influence on the susceptibility is very weak, even for larger anisotropic contributions. The magnetization is more strongly influenced, but the very strong anisotropic components of approximately half the isotropic components, that would be necessary to smear out the magnetization steps, appear unrealistic.

The same is true for antisymmetric anisotropic exchange; the case study is shown in Figure 7. We investigated several orientations of the DM vectors. Shown is the symmetric case where the DM vectors point radially outwards at each bond. Here the anisotropic components would also have to be half of the magnitude of their isotropic counterparts in order to sufficiently smear out the magnetization steps.

Both scenarios appear to be excluded on the grounds of the simple estimate that the strength of the DM interaction is usually of the order of $\Delta g/g \cdot J$, and the strength of the anisotropic symmetric exchange of the order of $(\Delta g/g)^2 \cdot J$. From the splitting of the EPR peak we estimate $\Delta g/g \approx 0.02$, which renders both interactions virtually zero.

As a third scenario we investigated models with distributions of exchange interactions associated with a substantial amount of site and bond disorder. Since, the variation of the exchange coupling cannot be determined by experimental means, we model this distribution by a flat distribution. For this purpose, the nearest neighbour exchange interactions vary around the mean J according to a uniform box distribu-

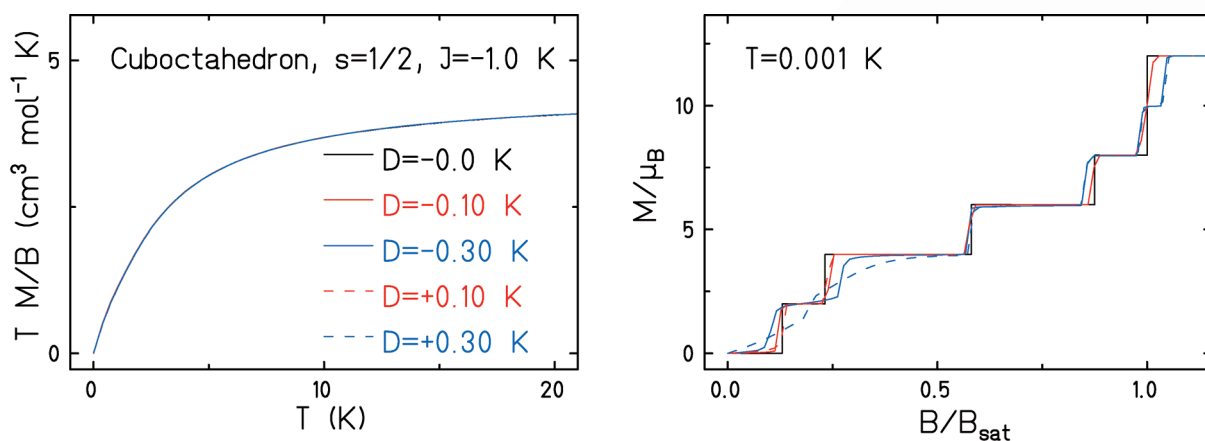


Figure 7. Theoretical low-field ($B=0.1 \text{ T}$) magnetic susceptibility and low-temperature ($T=0.001 \text{ K}$) magnetization of a regular cuboctahedron with antisymmetric exchange between nearest-neighbour spins.

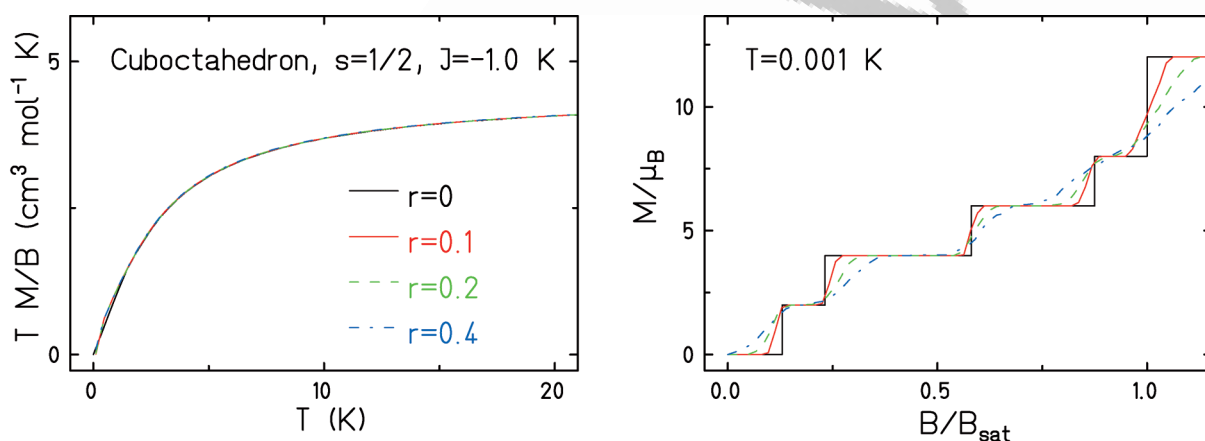


Figure 8. Theoretical low-field ($B=0.1 \text{ T}$) magnetic susceptibility and low-temperature ($T=0.001 \text{ K}$) magnetization of a regular cuboctahedron with random exchange between nearest-neighbour spins.

tion^[8] over the interval $[(1-r)J, (1+r)J]$. We generated 100 realizations for each parameter r . As Figure 8 shows using this model the magnetization is smeared out, although again a rather broad distribution with a width of at least $r=0.4$ would be needed.

For all three scenarios, even when going to the extremes, the quality of the fitting of the magnetic observables remains poor. Most importantly, none of the models comes close to the specific heat data. Since we assumed nearest-neighbour exchange interactions in all scenarios, this failure could result from more sophisticated patterns of interactions being present, but not obvious. This leaves as a final explanation the presence of intermolecular interactions between molecules. Although such interactions are weak, even if the distances between cages in the extended structures of all three compounds are of the order of $3\text{--}5 \text{ \AA}$, respectively (Figures S1–6), they can be able to dominate observables at temperatures below a certain scale.^[12] But since we do not observe true ordering in the specific heat we think that the intermolecular interactions create correlated clusters of molecules on various

length scales which is compatible with a smeared out specific heat. The fact that a magnetic field of about 4 T is sufficient to restore a molecule-like behaviour allows us to estimate the magnitude of the intermolecular interactions which we think is of the order of 5 K .

Our failure to explain the magnetic observables of the investigated cages with a simple and “obvious” model is both fascinating and astonishing for various reasons. We are used to explicitly trusting crystallography (even when taken at higher temperatures); magneto-structural correlations are well known and well-established for Cu^{II} compounds,^[13] and we assume that the present compounds should behave like highly symmetric clusters in the strong Heisenberg exchange limit. A pitfall in our assumptions might be that magneto-structural correlations work well for small molecules, like dimers, but may fail when dealing with much larger, more intricate cages such as keplerates. Crystallography measures a diffraction pattern from an array of very similar, but not identical, molecules. The molecular packing and metric parameters will also change with temperature, and not all parameters will change in an identical

way. Therefore, even where the apparent crystallographic symmetry is very high, individual molecules may differ from their neighbours in small ways, hidden by the estimated standard deviations of the metric parameters. The correlations between J_{CuCu} and angles suggest a strong dependence, and hence even the standard deviations would produce a range of J values. Equally, the structures were recorded at $T \approx 120\text{--}30\text{ K}$, above the temperature of the (H) measurements. The result is therefore that it is probably inevitable that in large Cu^{II} cages, the high symmetry of the crystallographic measurements is not reflected in the physical measurements. A lack of solubility and an inability to make the fully diamagnetic versions of the cages precludes any dilution studies. In addition, the influence of intermolecular interactions on magnetic observables at low temperatures is certainly underestimated. Under these circumstances it appears as a miracle that one observes magnetization steps at all in other compounds. We also note that similarly featureless $M(H)$ behaviour has recently been reported for a $\{\text{Cu}_{27}\}$ cage.^[8]

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Keywords: copper · cuboctahedron · frustration · keplerates · molecular symmetry

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- [5] a) Crystallographic data for 1. $\text{Cu}_{12}\text{Mg}_6\text{C}_{24}\text{H}_{44}\text{O}_{61}$, light blue prism ($0.19 \times 0.13 \times 0.05\text{ mm}$), $M_r = 2265.55$, Orthorhombic, $Pnmm$, $a = 17.1724(13)\text{ Å}$, $b = 17.4550(13)\text{ Å}$, $c = 17.1671(13)\text{ Å}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 5145.7(7)\text{ Å}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.462\text{ Mg/m}^3$, $\mu = 2.556\text{ mm}^{-1}$, $\lambda = 0.71075\text{ Å}$, $T = 100\text{ K}$; 36430 collected reflections, 4212 unique ($R_{\text{int}} = 0.0384$). The final R_1 ($I > 2\sigma(I)$) = 0.1028, wR_2 (aII) = 0.2862, $\text{GoF} = 1.056$, CCDC depository number: 1051236; b) Crystallographic data for 2. $\text{C}_{194}\text{H}_{411}\text{Cu}_{40}\text{N}_{19}\text{O}_{130}$, light blue blocks ($0.04 \times 0.05 \times 0.06\text{ mm}$), $M_r = 7631.99$, Triclinic, $P-1$, $a = 19.0840(3)\text{ Å}$, $b = 19.8326(4)\text{ Å}$, $c = 21.1877(4)\text{ Å}$, $\alpha = 90.8108(15)^\circ$; $\beta = 93.0325(14)^\circ$; $\gamma = 90.6441(15)^\circ$, $V = 5145.7(7)\text{ Å}^3$, $Z = 1$, $\rho_{\text{calc}} = 1.583\text{ Mg/m}^3$, $\mu = 2.676\text{ mm}^{-1}$, $\lambda = 0.71073\text{ Å}$, $T = 150.05(16)\text{ K}$; 85205 collected reflections, 32550 unique ($R_{\text{int}} = 0.0354$). The final R_1 ($I > 2\sigma(I)$) = 0.0451, wR_2 (aII) = 0.1069, $\text{GoF} = 1.033$, CCDC depository number: 1408858; c) Crystallographic data for 3. $\text{C}_{93}\text{H}_{167}\text{Al}_6\text{Cu}_{12}\text{Eu}_6\text{NO}_{89.5}$, blue cubes ($0.08 \times 0.08 \times 0.08\text{ mm}$), $M_r = 4562.35$, Cubic, $Ia-3d$, $a = b = c = 41.3329(2)\text{ Å}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 70613.3(10)\text{ Å}^3$, $Z = 16$, $\rho_{\text{calc}} = 1.717\text{ Mg/m}^3$, $\mu = 17.556\text{ mm}^{-1}$, $\lambda = 1.54184\text{ Å}$, $T = 100\text{ K}$; 185351 collected reflections, 6053 unique ($R_{\text{int}} = 0.1335$). The final R_1 ($I > 2\sigma(I)$) = 0.0793, wR_2 (aII) = 0.2399, $\text{GoF} = 1.085$, CCDC depository number: 1408857.
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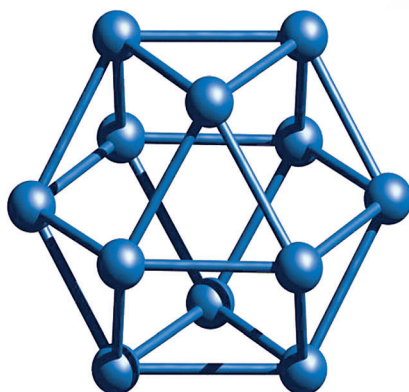
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New copper keplerates are reported, with physical studies indicating that even where very high molecular symmetry is found, the low-temperature physics does not necessarily reflect this symmetry



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